

Attorney Docket No. 83303  
Customer No. 23523

HIGH STRAIN PIEZO-POLYMER

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT (1) THOMAS S. RAMOTOWSKI, employee of the United States Government, (2) GEORGE J. KAVARNOS and (3) QIMING ZHANG, citizens of the United States of America, and residents of (1) Tiverton, County of Newport, State of Rhode Island, (2) New London, County of New London, State of Connecticut, and (3) State College, County of Centre, State of Pennsylvania, have invented certain new and useful improvements entitled as set forth above of which the following is a specification.

MICHAEL F. OGLO, ESQ.  
Reg. No. 20464  
Naval Undersea Warfare Center  
Division, Newport  
Newport, Rhode Island 02841-1708  
Tel: 401-832-4736  
Fax: 401-832-1231

I hereby certify that this correspondence is being deposited with the U.S. Postal Service as U.S. EXPRESS MAIL, Mailing Label No. EV326644805US  
In envelope addressed to: Commissioner for Patents, Alexandria, VA  
20231 on 21 November 2003  
(DATE OF DEPOSIT)

Michael F. Oglo  
APPLICANT'S ATTORNEY

21 November 2003  
DATE OF SIGNATURE

1 Attorney Docket No. 83303

2  
3 HIGH STRAIN PIEZO-POLYMER  
4

5 The present application is based on a Provisional  
6 Application, No. 60/428,167, which was filed on November 21,  
7 2002, and which is entitled HIGH STRAIN PIEZO-POLYMER by Thomas  
8 Ramotowski, George Kavarnos, and Qiming Zhang.  
9

10 STATEMENT OF GOVERNMENT INTEREST

11 The invention described herein may be manufactured and used  
12 by the Government of the United States of America for  
13 Governmental purposes without the payment of any royalty thereon  
14 or therefor.  
15

16 CROSS REFERENCE TO OTHER RELATED APPLICATIONS

17 None.  
18

19 BACKGROUND OF INVENTION

20 (1) Field of the Invention

21 This invention relates to a new class of terpolymers for  
22 use as high strain electrostrictive polymer films. More  
23 particularly, the invention relates to a class of  
24 electrostrictive terpolymers comprising vinylidene fluoride

(VDF), trifluoroethylene (TrFE) and at least one monomer having at least one bulky halogen atom side group. The monomer is preferably a chloro-monomer such as chlorofluoroethylene (CFE) or chlorotrifluoroethylene (CTFE). The chlorofluoroethylene (CFE) is preferably 1-chloro-2-fluoroethylene or 1-chloro-1-fluoroethylene.

## (2) Description of the Prior Art

Many research activities in the past decade have focused on vinylidene fluoride-trifluoroethylene (VDF-TrFE) copolymers with the goal of reducing the energy barrier for ferroelectric-paraelectric phase transition and generating large and fast electric-induced mechanical responses at ambient temperatures. The close connection between the crystalline structure and electric properties led to many attempts to alter copolymer morphology by mechanical deformation, electron-radiation, crystallization, etc.

One of the main methods of processing or converting polymers into electrostrictive polymers has been by electron irradiation. Electron irradiation is the exposure to high-energy electrons. Electron irradiation of polymer films serves to break up the large crystalline regions of the polymer films into polar micro-regions resulting in a high-strain electrostrictive material.

Electrostriction is the high strains displayed by certain materials when stressed by electric fields. The magnitude of the electrostrictive strain can be described by the following equation:

$$S = QP^2,$$

where  $Q$  is the electrostrictive coefficient and  $P$  is the polarization of the material.

Ferroelectric polymers such as poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] films, previously annealed, can be converted into electrostrictive polymers by exposure to high energy electron bombardment. Electron bombardment of high crystalline P(VDF-TrFE) films break up the long-range ferroelectric region into polar micro-domains thereby broadening the ferroelectric-to-paraelectric transition and moving the transition to a lower temperature where high strains can be observed when the films are driven by large electric fields. These strains in the polymer films caused by electron bombardment and the ensuing effects on the polymer structure can be characterized by differential scanning calorimetry, X-ray diffraction and infrared spectroscopy.

Ferroelectric polymers can contain various *trans* and *gauche* configurations, including form I( $\beta$ ), II( $\alpha$ ), and III( $\gamma$ ). In form I, the chains exhibit an all-*trans* configuration. In form II, the packed chains exhibit the *tgtg'* ( $t$  = *trans*;  $g, g'$  = *gauche*)

1 conformation, resulting in a nonpolar crystallite. In form III,  
2 the chains exhibit  $tttg'ttg'$  conformation, resulting in a  
3 monoclinic lattice and a polar cell.

4 Electron irradiation, i.e., electron bombardment, of these  
5 ferroelectric polymers converts the polar all-trans form I( $\beta$ ),  
6 long-range ferroelectric regions of annealed P(VDF-TrFE) films  
7 into nanoregions consisting of coexisting I( $\beta$ ), II( $\alpha$ ), and  
8 III( $\gamma$ ) crystallites, preferably having Curie (polar-nonpolar  
9 crystalline phase) transition at ambient temperatures. The  
10 polarization of these regions give rise to a macroscopic  
11 polarization and increase in the dielectric constant. The  
12 macroscopic polarization provides an increase in dielectric  
13 constant, large strains, much improved coupling constants and  
14 large ( $d_{33}$ ) signal piezoelectric constant.

15 Where the electrostrictive strains of materials are high  
16 enough, materials having this property offer great promise in  
17 applications such as sensors, underwater sonar transduction,  
18 polymeric actuators, artificial muscles, and robotics. In these  
19 and other applications, the high strain electrostrictive  
20 materials provide higher/greater sensitivity, more powerful  
21 signals and more efficient energy conversion.

22 However, electron irradiation, i.e., electron bombardment,  
23 is cumbersome and expensive. Electron irradiation is also a  
24 slow process because a large dose of radiation is needed to

1 achieve electrostrictive properties. Other disadvantages  
2 associated with using electron irradiation which cause it to be  
3 a slow process is that: (1) only a limited thickness of films  
4 can be irradiated at a time; (2) the electron beam used is  
5 narrow, while film size varies and can be much wider than the  
6 electron beam; and (3) a vast fluctuation in conditions may  
7 exist throughout the electron irradiation process.

8 The prior art discloses various polymers such as Nakamura  
9 et al., U.S. Patent No. 4,543,293, which is said to disclose a  
10 piezoelectric polymer comprising vinylidene fluoride,  
11 trifluoroethylene and vinyl fluoride.

12 Also known in the prior art is Pantelis, U.S. Patent No.  
13 4,557,880, which is said to disclose a piezoelectric film made  
14 from vinylidene fluoride and tetrafluoroethylene and/or  
15 trifluoroethylene.

16 Also known in the prior art is Sako et al., U.S. Patent No.  
17 4,577,005, which is said to disclose a polymeric dielectric  
18 material comprising a terpolymer which comprises vinylidene  
19 fluoride, trifluoroethylene and hexafluoropropylene that is heat  
20 treated.

21 Also known in the prior art is Preis, U.S. Patent No.  
22 4,778,867, which is said to disclose a ferroelectric random  
23

1 copolymer consisting essentially of vinylidene fluoride and  
2 trifluoroethylene that is heat treated.

3 Also known in the prior art is Inukai et al., U.S. Patent  
4 No. 5,087,679, which is said to disclose a polymeric dielectric  
5 which comprises vinylidene fluoride, trifluoroethylene and  
6 chlorotrifluoroethylene.

7 Also known in the prior art is Chung et al., U.S. Patent  
8 No. 6,355,749, which is said to disclose a ferroelectric  
9 terpolymer comprising vinylidene fluoride, trifluoroethylene and  
10 chlorotrifluoroethylene or hexafluoropropene.

11 Also known in the prior art is Gervasi et al., U.S. Pub.  
12 No. 2002/0132074, which is said to disclose a fluoroelastomer  
13 terpolymer comprising vinylidene fluoride, hexafluoropropylene  
14 and tetrafluoroethylene or chlorotrifluoroethylene.

15 Other ferroelectric and electrostrictive polymers and  
16 methods of altering polymer morphology may be known. However,  
17 these polymers and methods, along with those above, have various  
18 shortcomings. These shortcomings are addressed by the present  
19 invention. As such, the present invention provides  
20 electrostrictive polymers using an alternative method of  
21 altering copolymer morphology, without the need for electron  
22 irradiation.

## SUMMARY OF THE INVENTION

A primary objective of the present invention to produce an electrostrictive terpolymer such as vinylidene fluoride-trifluoroethylene-chlorofluoroethylene (VDF-TrFE-CFE), without utilizing electron irradiation, which may be used as an active material capable of generating sound in acoustic, underwater transducers and mechanical motion in actuator devices.

It is also a primary objective of the present invention to produce an electrostrictive terpolymer such as VDF-TrFE-CFE which may be used as a replacement for electron irradiated high-strain P(VDF-TrFE) films.

It is also a primary objective of the present invention to produce an electrostrictive terpolymer such as VDF-TrFE-CFE which has *gauche*-type conformational defects along the polymer chain which results in a broad distribution of polarizations that favor higher electrostrictive strains than current electrostrictive polymers.

It is also an objective of the present invention to produce an electrostrictive terpolymer which exhibits larger mechanical strains than known in the art.

It is also an objective of the present invention to process an electrostrictive terpolymer such as VDF-TrFE-CFE which is less expensive and less cumbersome than current electrostrictive



1 materials and methods of making those electrostrictive  
2 materials.

3 In accordance with the present invention there is provided  
4 a new class of terpolymers for use as high strain  
5 electrostrictive polymer films. More particularly, the  
6 invention relates to a class of terpolymers comprising at least  
7 three monomers wherein their reaction produces terpolymers  
8 having high electrostrictive properties. Specifically, the  
9 electrostrictive terpolymers comprise vinylidene fluoride (VDF),  
10 trifluoroethylene (TrFE) and at least one monomer having at  
11 least one halogen atom side group. The monomer is preferably an  
12 ethylene-based monomer and preferably selected to favor *gauche*-  
13 type linkage along the polymer backbone. The halogen atom side  
14 group is preferably bulky or large enough to move or cause  
15 adjacent polymer chains to be farther apart from or away from  
16 each other than in the absence of such halogen atom side group,  
17 but not so large that it would inhibit polymer crystallites from  
18 forming. The monomer is preferably a chloro-monomer such as  
19 chlorofluoroethylene (CFE). The chlorofluoroethylene (CFE) is  
20 preferably 1-chloro-2-fluoroethylene or 1-chloro-1-  
21 fluoroethylene. The monomer may also be chlorotrifluoroethylene  
22 (CTFE), but CTFE favors *trans*-type linkage instead of *gauche*-  
23 type linkage. As such, electrostrictive terpolymers comprising  
24

1 CFE have higher electrostrictive strains than terpolymers  
2 comprising CTFE.

3 Other details of the high strain polymer of the present  
4 invention, as well as other objects and advantages attendant  
5 thereto, are set forth in the following detailed description and  
6 accompanying drawings.

#### 8 BRIEF DESCRIPTION OF THE DRAWINGS

9 Referring now to the drawings:

10 FIG. 1 is a graph illustrating the energy of *gauche* forms  
11 and all-trans forms of a chlorinated chain polymer compared to a  
12 non-chlorinated chain polymer;

13 FIG. 2 are graphs comparing the dihedral distributions  
14 following a molecular dynamic simulation of 100 monomer chains  
15 of  $\text{-ClFC-CH}_2\text{-}$  (left) and  $\text{-ClFC-CF}_2\text{-}$  (right);

16 FIG. 3 is a graph illustrating the dielectric constant  
17 versus temperature for VDF-TrFE-CFE terpolymers of the present  
18 invention at various frequencies;

19 FIG. 4 is a graph comparing the polarization versus the  
20 applied electric field for VDF-TrFE-CFE terpolymers of the  
21 present invention;

22 FIG. 5 is a graph illustrating the strain (in %) versus the  
23 magnitude of an electric field (in MV/m) of two VDF-TrFE-CFE  
24 terpolymers of the present invention; and

1        FIG. 6 is a graph illustrating the modulus and mechanical  
2 loss tangent versus temperature for various frequencies for VDF-  
3 TrFE-CFE terpolymers of the present invention.

#### 5                    DESCRIPTION OF THE PREFERRED EMBODIMENTS

6        Materials having high electrostrictive strains  
7 are beneficial for use in applications such as sensors,  
8 underwater sonar transduction, polymeric actuators, artificial  
9 muscles, and robotics for providing higher/greater sensitivity,  
10 more powerful signals and more efficient energy conversion. As  
11 such, new electrostrictive materials and methods of synthesizing  
12 these electrostrictive materials are being developed to replace  
13 electron irradiated high strain polymer vinylidene fluoride-  
14 trifluoroethylene [P(VDF-TrFE)] films while possessing all of  
15 the electrostrictive properties of the electron irradiated high  
16 strain P(VDF-TrFE) films.

17        Accordingly, the present invention is a new class  
18 of terpolymers for use as high strain electrostrictive polymer  
19 films. More particularly, the invention is a class of  
20 electrostrictive terpolymers comprising vinylidene fluoride  
21 (VDF), trifluoroethylene (TrFE) and at least one monomer having  
22 at least one halogen atom side group. The monomer is preferably  
23 an ethylene-based monomer and preferably selected to favor  
24 *gauche*-type linkage along the polymer backbone.

1       The halogen atom side group is preferably bulky or large  
2 enough to move or cause adjacent polymer chains to be farther  
3 apart from or away from each other than in the absence of such  
4 halogen atom side group, but not so large that it would inhibit  
5 polymer crystallites from forming. In a preferred embodiment,  
6 the halogen atom side group in the monomer is preferably  
7 chlorine. The introduction of chlorine in the polymer chain  
8 affects crystal packing during annealing by acting as a defect  
9 that disrupts the polar all-trans long-range regions in the  
10 polymer into nanoregions. Specifically, the introduction of  
11 chlorine atoms into the polymer chains creates conformational  
12 defects that provide the mechanism to break up the all-trans  
13 long-range crystalline regions and disrupt the long-range  
14 ferroelectric order, thereby converting these regions into  
15 nanoregions.

16       The chlorine forces the crystalline dimensions to expand  
17 and distort to accommodate the chlorine atoms. The disrupted  
18 polar regions can be regarded as distorted defect structures  
19 which give rise to random polar fields and electrostrictive  
20 properties such as high strains. This effect is attributed to  
21 the large van der Waals radius of the chlorine atom.  
22 Specifically, the van der Waals radius of chlorine is 1.8 Å.

23       In a preferred embodiment, a chloro-monomer which can  
24 convert VDF-TrFE polymer films into high-strain electrostrictive

1 films is chlorofluoroethylene (CFE), preferably 1-chloro-2-  
2 fluoroethylene or 1-chloro-1-fluoroethylene. The chloro-monomer  
3 may also be chlorotrifluoroethylene (CTFE), but CTFE favors  
4 *trans*-type linkage. As such, electrostrictive terpolymers  
5 comprising CFE have higher electrostrictive strains than  
6 terpolymers comprising CTFE. FIG. 2 illustrates the dihedral  
7 distribution of monomer chains of chlorofluoroethylene  
8 (-ClFC-CH<sub>2</sub>-) and chlorotrifluoroethylene (-ClFC-CF<sub>2</sub>-). As shown,  
9 chlorofluoroethylene (-ClFC-CH<sub>2</sub>-) has higher frequencies at  
10 *gauche*-type linkages, whereas chlorotrifluoroethylene  
11 (-ClFC-CF<sub>2</sub>-) has higher frequencies at *trans*-type linkages.

12 A chloro-monomer added to the VDF-TrFE copolymer provides  
13 higher electrostrictive strains than non-chloro-monomers such as  
14 hexafluoropropylene (HFP), which contains a trifluoromethyl side  
15 group. The trifluoromethyl group is too large and too bulky and  
16 gets annealed out of the crystallites. Because of the large  
17 size of the trifluoromethyl group, HFP does not favor *gauche*-  
18 type linkage along the polymer chain. As such, HFP produces  
19 lower electrostrictive strains than the chloro-monomer in the  
20 present invention when added to P(VDF-TrFE).

21 Even if the amount of HFP was varied, these results do not  
22 change. If a small amount of HFP is used to form the  
23 terpolymer, some of the trifluoromethyl groups may temporarily  
24 be trapped within the crystallites, but over time, those groups

1 will be annealed out. As such, its performance decreases over  
2 time. If a large amount of HFP is used to form the terpolymer,  
3 the increased amount of HFP added to the VDF-TrFE copolymer  
4 greatly reduces crystallinity, which leads to low polarization  
5 and low strains. Accordingly, adding HFP to the VDF-TrFE  
6 copolymer does not provide optimum electrostrictive properties.

7 As provided by the terpolymer of the present invention and  
8 as shown in FIG. 1, adding a chloro-monomer which favors *gauche*-  
9 type linkage to the VDF-TrFE copolymer synthesizes a terpolymer  
10 having higher energy, i.e., higher electrostrictive properties  
11 such as higher electrostrictive strains, than a terpolymer  
12 synthesized by adding a non-chloro-monomer, such as HFP, as the  
13 monomer. This result is due to the chlorine group on the  
14 chloro-monomer being not too large to inhibit polymer  
15 crystallites from forming, but large enough to push or move the  
16 polymer chains farther apart from or away from each other than  
17 in the absence of such chlorine group, thereby distorting the  
18 polymer crystal lattice. The chloro-monomer CFE of the  
19 preferred embodiment of the present invention favors *gauche*-type  
20 linkage along the polymer chain which produces higher  
21 electrostrictive strains.

22 While CTFE is a chloro-monomer, it favors *trans*-type  
23 linkage along the polymer chain and does not result in the  
24 highest electrostrictive strains possible, as shown in FIG. 2.

1 Alternatively, CFE is a chloro-monomer wherein its chlorine  
2 group is large enough to push or move the polymer chains farther  
3 apart from or away from each other than in the absence of such  
4 chlorine group, thereby distorting the polymer crystal lattice,  
5 but also favors the performance-enhancing *gauche*-type polymer  
6 chain configurations, as shown in FIG. 2. Therefore, the  
7 terpolymer VDF-TrFE-CFE of the present invention has side groups  
8 (fluorine and chlorine) which are large enough to cause a  
9 crystal lattice disruption, but small enough not to seriously  
10 degrade crystallinity, thereby resulting in performance-  
11 enhancing *gauche*-type polymer chain configurations having higher  
12 polarization and higher electrostrictive strains.

13 The properties of the VDF-TrFE-CFE terpolymers were  
14 determined by molecular dynamics simulations and  
15 experimentation. The results of these simulations and  
16 experimentation are shown in FIGS. 3-6. As such, the  
17 terpolymers of the present invention exhibit a high dielectric  
18 constant at ambient temperatures as shown in FIG. 3. The  
19 terpolymers of the present invention also exhibit large  
20 electrical responses in ambient temperatures under electric  
21 fields. As such, FIG. 4 illustrates the polarization versus the  
22 applied electric field of the VDF-TrFE-CFE terpolymers. FIG. 5  
23 illustrates the strains (in %) versus the electrical field (in  
24 MV/m) for two examples of the terpolymers of the present

1 invention, as evidenced during simulations and experimentation.  
2 FIG. 6 illustrates the modulus (MPa) and mechanical loss tangent  
3 versus temperature for the VDF-TrFE-CFE terpolymers of the  
4 present invention.

5 The terpolymer VDF-TrFE-CFE is preferably synthesized from  
6 the polymerization of vinylidene fluoride (VDF),  
7 trifluoroethylene (TrFE) and chlorofluoroethylene (CFE),  
8 preferably either 1-chloro-2-fluoroethylene or 1-chloro-1-  
9 fluoroethylene. In a preferred embodiment of the terpolymer  
10 VDF-TrFE-CFE, the amount of vinylidene fluoride (VDF) used  
11 preferably ranges from about 65 mole % to about 71 mole %, more  
12 preferably from about 66 mole % to about 70 mole %, and most  
13 preferably from about 67 mole % to about 69 mole %. The amount  
14 of trifluoroethylene (TrFE) used preferably ranges from about 26  
15 mole % to about 33 mole %, more preferably from about 27 mole %  
16 to about 30 mole %, and most preferably from about 28 mole % to  
17 about 29 mole %. The amount of chlorofluoroethylene (CFE) used  
18 preferably ranges from about 1 mole % to about 6 mole %, more  
19 preferably from about 2 mole % to about 5 mole %, and most  
20 preferably from about 3 mole % to about 4 mole %. For example,  
21 a VDF-TrFE-CFE terpolymer of the present invention may comprise  
22 68 mole % VDF, 28 mole % TrFE and 4 mole % CFE.

23 The terpolymer is then subjected to either solvent casting  
24 or extrusion and annealed, i.e., heated and then cooled. After



1 either solvent casting or extrusion and annealing, thin films of  
2 VDF-TrFE-CFE are electrostrictive, i.e., the films exhibit large  
3 mechanical strains when placed in an oscillating electric field.

4 Since crystallization into large regions is prevented, as  
5 described above, the terpolymer VDF-TrFE-CFE anneals as a  
6 disordered material with random defect fields underlying its  
7 electrostriction. As such, the electrostrictive terpolymer VDF-  
8 TrFE-CFE possesses *gauche*-type conformational defects along the  
9 polymer chain that result in a broad distribution of  
10 polarizations that favor higher electrostrictive strains than  
11 other known electrostrictive polymers.

12 The electrostrictive terpolymer VDF-TrFE-CFE of the present  
13 invention can be used as an electrostrictive material in its  
14 annealed state without being subjected to electron irradiation.  
15 Since the chloro-monomer added to the P(VDF-TrFE) produces  
16 electrostrictive properties, i.e., electrostrictive strains,  
17 greater than those strains produced by electron irradiation of  
18 P(VDF-TrFE), the VDF-TrFE-CFE terpolymer of the present  
19 invention solves the problems associated with processing  
20 polymers into electrostrictive materials by electron  
21 irradiation.

22 The electrostrictive terpolymer VDF-TrFE-CFE of the present  
23 invention is also conformable, robust, and chemically durable  
24 which makes it good for use in hostile environments. The

1 electrostrictive terpolymer VDF-TrFE-CFE may preferably be used  
2 as an active material capable of generating sound in acoustic,  
3 underwater transducers and mechanical motion in actuator  
4 devices. Specifically, the electrostrictive terpolymer VDF-  
5 TrFE-CFE is applicable in sensors, sonars in submarines, in  
6 actuators and in smart skins of vehicles or materials which are  
7 used to sense vibration and control noise, such as in stealth  
8 jets and submarines. In these and other applications, the  
9 electrostrictive terpolymer provides higher/greater sensitivity,  
10 more powerful signals and more efficient energy conversion.

11 The processing of the electrostrictive terpolymer VDF-TrFE-  
12 CFE of the present invention is less expensive and less  
13 cumbersome than processing electrostrictive polymers by electron  
14 irradiation or other known technologies. In addition, the  
15 processing of the electrostrictive polymer VDF-TrFE-CFE of the  
16 present invention produces electrostrictive polymers which  
17 exhibit larger mechanical strains than other known  
18 electrostrictive materials.

19 The exemplary embodiments herein disclosed are not intended  
20 to be exhaustive or to unnecessarily limit the scope of the  
21 invention. The exemplary embodiments were chosen and described  
22 in order to explain the principles of the present invention so  
23 that others skilled in the art may practice the invention. As  
24 will be apparent to one skilled in the art, various

1 modifications can be made within the scope of the aforesaid  
2 description. Such modifications being within the ability of one  
3 skilled in the art form a part of the present invention and are  
4 embraced by the appended claims.